

PATENT SPECIFICATION

(11) 1424747

1424747

- (21) Application No. 40528/73 (22) Filed 28 Aug. 1973
 (23) Complete Specification filed 27 Aug. 1974
 (44) Complete Specification published 11 Feb. 1976
 (51) INT CL² C07D 307/60
 (52) Index at acceptance
 C2C 1471 215 247 253 25Y 305 30Y 351 352 369 386
 401 40Y 635 761 TQ
 (72) Inventor JEAN STEPHAN EDMOND RAMIOULLE



(54) METHOD AND APPARATUS FOR THE CONTINUOUS DEHYDRATION OF MALEIC ACID

(71) We, UCB, of 4, Chaussée de Charleroi, Saint-Gilles-lez-Bruxelles, Belgium, a Body Corporate organised under the laws of Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a new method of dehydrating maleic acid to maleic anhydride by a continuous process and is also concerned with an apparatus for carrying out this new method. More particularly, the present invention is concerned with the recovery of maleic anhydride from an aqueous solution of maleic acid formed in the production of maleic anhydride by the catalytic oxidation of aliphatic and aromatic hydrocarbons, such as butane, butene and benzene.

In the effluent of a maleic anhydride synthesis reactor, the maleic anhydride vapours are very considerably diluted by a mixture of inert gases, such as nitrogen and unconsumed oxygen. Although the vapour pressure of maleic anhydride at its melting point is only a few millimetres of mercury, the dilution is such that at least 15% of the maleic anhydride leaving the reactor is not condensed by cooling and, therefore, can be recovered practically only by absorption in a solvent, generally water. In other words, in practically all processes actually used on an industrial scale, at least part of the synthesised maleic anhydride is finally in the form of an aqueous solution of maleic acid.

The reconversion of the (aqueous) solution of maleic acid into maleic anhydride by a continuous process encounters various difficulties, due to the presence of impurities. Some of these impurities originate from the reactor for the catalytic oxidation of hydrocarbons into maleic anhydride and comprise, for example, entrained catalyst, products of incomplete oxidation, such as benzoquinone and resinous materials, the remainder of the impurities formed in the course of the actual reconversion of maleic acid into maleic an-

hydride comprising principally fumaric acid. All these impurities gradually accumulate in the apparatus in the course of time and the moment arrives when production must be stopped because clogging occurs and the transmission of heat becomes poorer and poorer because of the deposition of these impurities on the heat exchange surfaces. This cleaning operation is very laborious for the maintenance staff, while, in addition, the closing down of the installation constitutes a substantial loss of production and material.

In our Belgian Patent Specification No. 745,029, we have solved the problem of eliminating the impurities (fumaric acid, resins and the like) in a continuous process by a method consisting in only partly converting the maleic acid into the corresponding anhydride and treating the unconverted maleic acid, which entrains these impurities, with water in order, in this way, to form a solid phase composed of fumaric acid and other insoluble impurities and an aqueous liquid phase containing the dissolved maleic acid. The solid phase is eliminated from the system by filtration and the aqueous filtrate of maleic acid is recycled to the process. This process is satisfactory, provided that the operating criteria of the dehydrator for the partial conversion of maleic acid into the corresponding anhydride (dehydration pressure and temperature, residence time and the like) are scrupulously respectively, these criteria varying, depending upon the freshness of the synthesis catalyst, the composition of the maleic acid subjected to dehydration and the like. It would be very advantageous to provide a process enjoying all the advantages of the process described in Belgian Patent Specification No. 745,029, while possessing greater flexibility of operation. This is what constitutes the object of the present invention.

The present invention provides a continuous process for the preparation of maleic anhydride from an aqueous solution of maleic acid formed in the production of maleic anhydride by the catalytic oxidation of aliphatic

50
55
60
65
70
75
80
85
90
95

or aromatic hydrocarbons, with the continuous elimination of the impurities which accompany this maleic acid solution or which are subsequently formed in the course of the conversion of maleic acid into maleic anhydride, which comprises the following stages:

- (a) the starting aqueous solution of maleic acid is continuously heated in a concentration zone kept at a temperature of 100—150°C. and at a pressure of 400—700 mm.Hg. in order to obtain molten maleic acid containing 0—10% by weight of water and water vapour, said water vapour being washed in order to recover the entrained maleic acid, the aqueous solution of maleic acid thus formed being fed to stage (c);
- (b) the molten maleic acid obtained in stage (a) is fed continuously to a conversion zone kept at a temperature of 115—165°C. and at a pressure of 40—200 mm.Hg. and containing, on the one hand, a liquid suspension consisting of a reaction mixture containing 1—20% by weight of maleic acid, 0—30% by weight of fumaric acid, 99—55% by weight of maleic anhydride and 0—5% by weight of resinous residues and, on the other hand, a purified gaseous phase containing maleic anhydride and water vapour, the amount of molten maleic acid added in an hour to the said reaction mixture representing from 10 to 50% of the weight of said reaction mixture;
- (c) part of said reaction mixture, representing from 0.5 to 5% by weight of said reaction mixture per hour, is continuously or semi-continuously taken off and fed to a dissolution and filtration zone, in which it is suspended in the aqueous solution of maleic acid coming from stages (a) and (d), the suspension thus obtained being filtered in order to separate a solid cake of fumaric acid and resinous residues, which is discharged from the system, and a liquid filtrate consisting of an aqueous solution of maleic acid, which is recycled to the starting aqueous solution of maleic acid;
- (d) the gaseous phase produced in stage (b) is continuously condensed at a temperature above the dew point of the water vapour present, the condensate thus obtained being maleic anhydride with a purity of at least 99%, which is collected as the product of the process, while the residual water vapour, which still contains entrained maleic anhydride, is washed with water in order to form an aqueous solution of maleic acid, which is recycled to stage (c).

By "starting aqueous solution of maleic acid" is meant the aqueous solution of maleic acid obtained by washing the reaction gases, either directly at the outlet of the synthesis reactor or at the outlet of the maleic anhydride condenser, when this device is used; furthermore, the "starting aqueous solution of maleic

acid" comprises the aqueous solutions of maleic acid formed in stages (a), (c) and (d) of the process. In general, the total maleic acid titre of the "starting aqueous solution of maleic acid" is between about 250 and 500 g./litre.

By "resinous residues" are to be understood, in the context of the present invention, the various impurities existing in the system, with the exception of fumaric acid. These impurities comprise (1) the oxidation catalyst entrained from the synthesis reactor by the reaction gases, (2) products of partial oxidation of the hydrocarbon material used in the synthesis, for example benzoquinone, and (3) resinous products which are formed in the synthesis reactor and/or in the dehydration of the molten maleic acid in stage (b) of the process.

Stage (a).

The concentration zone mentioned in (a) may comprise one or more evaporator devices of any kind, preference being given, however, to so-called thin layer evaporators. In this concentration zone, the temperature is kept between 100 and 150°C. and preferably at about 135°C., while the pressure is kept between 400 and 760 mm.Hg. and preferably at about 500 mm.Hg., in order to reduce the water content of the maleic acid to 0—10% by weight. For the good performance of the process, it is advantageous to lower the water content of the solution to the lowest possible value; dehydration may even be continued slightly beyond 100%, i.e. until the beginning of the conversion of maleic acid into maleic anhydride. The residence time of the maleic acid in the concentration zone is advantageously from 0.1 to 5 minutes and is preferably less than 1 minute. The partially or completely dehydrated maleic acid arrives at the outlet of the concentration zone in a liquid state and its temperature is between 125 and 150°C. Because of the moderate operating conditions applied in the concentration zone and because of the short residence time, the presence of fumaric acid in the maleic acid thus obtained is practically undetectable.

The water vapour eliminated during the concentration of the aqueous maleic acid solution into substantially anhydrous molten maleic acid entrains a certain amount of maleic acid. For this reason, the water vapour is passed into a washer in order to recover the entrained maleic acid; the aqueous solution of maleic acid obtained in this manner is used in stage (c).

Stage (b).

The molten maleic acid obtained in stage (a) is fed to the conversion zone (b) which comprises a large capacity still-dehydrator, i.e. a vessel provided with a supply pipe for

molten maleic acid, heating means, a vacuum connection pipe which serves at the same time as a pipe for the elimination of a vaporised mixture of water and maleic anhydride and a purge pipe for removing part of the reaction mixture contained in the still-dehydrator. The still-dehydrator may optionally contain agitation means and a maleic anhydride inlet pipe.

The still-dehydrator contains a reaction mixture, the composition of which must be maintained within limits which are critical for the good performance of the process. We have found that this reaction mixture must contain from 1 to 20% by weight of maleic acid, 99 to 55% by weight of maleic anhydride, 0 to 30% by weight of fumaric acid and 0 to 5% by weight of resinous residues. There are various ways of keeping the composition of the reaction mixture within the limits defined above. Thus, the percentage of maleic acid can be kept within the limits indicated by suitably adjusting the supply flow of molten maleic acid coming from stage (a); as a rule, when the reaction mixture has reached its stationary state within the composition limits indicated above, the hourly flow of molten maleic acid represents 10 to 50% of the weight of the reaction mixture in the still-dehydrator. In other words, the residence time of the molten maleic acid in the still-dehydrator is from 2 to 10 hours.

As the result of our investigations, we have found that a relationship also exists between the maleic acid content and the content of resinous residues in the reaction mixture, the maleic acid content increasing parallel with the increase of the content of resinous residues. This phenomenon appears to be connected with the fact that the resinous residues retard the conversion of maleic acid into maleic anhydride, while also reducing the heat exchange capacity of the still-dehydrator. As the resinous residues accumulate in the still-dehydrator in proportion as production proceeds, according to the present invention, provision is made for continuously or discontinuously purging the still-dehydrator, the amount purged representing from 0.5 to 5% by weight of the reaction mixture per hour, so as to keep the content of resinous residues within the limits indicated above.

The fumaric acid which is formed in the still-dehydrator also accumulates in the apparatus in the same way as the resinous residues and it is for this reason that the purge effected in order to reduce the content of resinous residues serves at the same time to eliminate the excess of fumaric acid from the still-dehydrator, thus making it possible to keep the composition of the reaction mixture within the limits indicated above.

The maleic anhydride content of the reaction mixture is governed by the operating conditions, the latter preferably comprising

a temperature between about 115 and about 165°C. and a pressure between about 40 and about 200 mm.Hg. when the stationary state of the composition of the reaction mixture has been reached. The maleic anhydride, which is continuously formed in the still-dehydrator at the expense of the maleic acid introduced, is eliminated in the form of a gaseous mixture of maleic anhydride and water.

Various methods are available for forming the reaction mixture. Thus, maleic acid from stage (a) can simply be added to the still-dehydrator until the latter is filled to its normal level; under the conditions of temperature and pressure prevailing in the still-dehydrator, the maleic acid is progressively converted into maleic anhydride and the introduction of maleic acid is finally so adjusted that the reaction mixture has the desired contents of maleic acid and maleic anhydride. As soon as the contents of fumaric acid and resinous residues of the mixture become too high, the continuous or discontinuous purging of the reaction mixture is effected in the manner explained above. Another possible procedure comprises introducing maleic anhydride of any origin into the still-dehydrator in advance and commencing the introduction of maleic acid coming from stage (a), while operating under the conditions of temperature and pressure specified above. Another way of forming the reaction mixture in the still-dehydrator consists in temporarily or continuously taking crude maleic anhydride from maleic anhydride condensers which are installed at the outlet of the synthesis reactor and feeding it to the still-dehydrator.

Stage (c).

Stage (c) of the process of the present invention deals with the elimination of the fumaric acid and resinous residues from the reaction mixture leaving the still-dehydrator in stage (b) through the purge pipe and, at the same time, recovering the maleic acid and/or maleic anhydride contained in the purged reaction mixture.

For this purpose, the purged reaction mixture is passed into a mixer in which the aqueous solution of maleic acid produced in stages (a) and (d) is added. The maleic acid and/or maleic anhydride contained in the purged reaction mixture is or are dissolved, while the fumaric acid and resinous residues remain insoluble and the aqueous suspension thus formed is passed to a conventional filtration apparatus in order to separate it into a solid filter cake and a liquid filtrate. The filter cake, which contains the fumaric acid and the resinous products, is washed and then removed from the system as production residue; if desired, the removal of the fumaric acid from it may be contemplated. The filtrate,

together with the filter cake washing liquid, consists of an aqueous solution of maleic acid, which is returned to the starting aqueous solution of maleic acid.

5 Stage (d).

The purified gaseous phase obtained in stage (b), which contains maleic anhydride and water vapour, is passed to a condensation zone in which, on the one hand, the maleic anhydride is condensed at a temperature higher than the dew point of the water vapour contained in this phase, and, on the other hand, the uncondensed portion of the gaseous phase is washed with water in order to recover, in the form of an aqueous solution of maleic acid, the maleic anhydride which remains in the uncondensed portion. The maleic anhydride condensed in this condensation zone constitutes the product of the present invention; its purity is at least 99% and its fumaric acid content is from 0 to 0.1%. However, in order to give it the degree of purity and degree of stability required by commercial standards, this product can easily be treated by suitable well known methods, particularly by vacuum distillation. The aqueous solution of maleic acid obtained by washing the gaseous phase is, in turn, passed to stage (c) of the process for the dissolution of the purged reaction mixture.

The process according to the present invention, which has just been described, offers very considerable advantages over the prior art:

35 in view of the fact that the impurities are continuously eliminated from the system, the process is truly continuous, in the sense that periodic cleaning of the installation for removal of incrustations caused by the accumulation of impurities is almost no longer required;

40 at the outlet of the installation, the maleic anhydride obtained by this process already has a purity of at least 99%, with a practically zero content of fumaric acid;

45 because the maleic anhydride and/or maleic acid is or are entirely recovered in stages (a), (c) and (d), in the form of an aqueous solution of maleic acid which is recycled to the starting aqueous solution of maleic acid, the only loss of raw material is the amount of maleic acid converted into fumaric acid. As the formation of fumaric acid, per hour of production, is at most 1.5% by weight of the starting maleic acid, the yield of maleic anhydride in the process of the present invention attains at least 98.5% of the theoretical value; moreover, the fumaric acid, which is thus recovered, after a possible purification by any known means, may be used, for example, in the production of unsaturated polyesters, various esters and the like;

60 the considerable mass of reaction mixture in the still-dehydrator of stage (b) constitutes

a thermal and chemical reserve, the fluctuations of which can easily be controlled, thus making it possible to achieve an entirely automatic operation of the installation;

because of the complete recycling of the washing liquids to the system, the problem of residual waters and pollution is reduced to a minimum, the only production residue being in practice the cake of fumaric acid and resinous residues produced in stage (c);

the performance of the process is flexible because it is possible to treat either a solution of maleic acid alone or a mixture of maleic acid solution and liquid maleic anhydride originating from maleic anhydride condensers (in this connection see the definition given previously of "starting aqueous solution of maleic acid" and the procedure for forming the reaction mixture in the still-dehydrator of stage (b));

this flexibility of the process makes it possible to treat not only products of the oxidation of benzene (in which case the condensation in solid or liquid form of the maleic anhydride at the outlet of the synthesis reactor is dependent on the overall economy of the investment and operation) but also products of the oxidation of butene or butane for which the possibility of condensation of maleic anhydride in solid or liquid form from these products is slight or non-existent.

In the accompanying drawing, one form of construction of an apparatus for carrying out the process of the present invention is shown diagrammatically.

Reference (1) indicates a washer containing the starting aqueous solution of maleic acid which is to be treated by the process of the present invention in order to recover the maleic anhydride. This solution is formed by washing the synthesis gases arriving through (2) either direct from a reactor (not shown) and, in this case, all the synthesized maleic anhydride is entirely converted into an aqueous solution of maleic acid, or is obtained from outlet gases of maleic anhydride condensers (not shown) and, in this case, liquid or solid maleic anhydride and an aqueous solution of maleic acid are, at the outset, produced simultaneously in the installation. The starting aqueous solution of maleic acid also contains aqueous solutions of maleic acid formed at various points in the installation (see below), which are recycled to the washer (1) through pipe (3). The starting aqueous solution of maleic acid is passed through pipe (4) to an evaporator (5), in which it is freed from practically all its water of dissolution by heating under reduced pressure ($T=100-150^{\circ}\text{C.}$; $P=400-760\text{ mm.Hg.}$). There is thus formed a vapour phase which still contains a certain amount of maleic acid and which leaves the evaporator (5) through pipe (6) and passes into a barometric washer (7) connected to a vacuum source (8), while liquid

for washing the vapour phase enters through pipe (9) and leaves through pipe (10). Molten maleic acid formed in the evaporator (5), is, in turn, passed through pipe (11) to a still-dehydrator (12) which contains a reaction medium comprising maleic acid, maleic anhydride, fumaric acid and resinous residues in the proportions indicated above. Maleic anhydride originating from maleic anhydride condensers (not shown) may optionally be introduced into the still-dehydrator (12) through pipe (13). In the still-dehydrator (12), which operates at elevated temperature and under vacuum ($T=115-165^{\circ}\text{C.}$; $P=40-200\text{ mm.Hg.}$), there is formed a gaseous mixture of purified maleic anhydride and water which leaves through pipe (14) and passes into condenser (15), from which the maleic anhydride is withdrawn from the process through pipe (16), while the water vapour, which entrains a certain amount of maleic anhydride, leaves at the top of the condenser (15) through pipe (17) and enters a barometric washer (18) connected by pipe (19) to a vacuum source (not shown), while the washing liquid enters the barometric washer (18) through pipe (20) and leaves it through pipe (21).

In order to effect the continuous elimination of the fumaric acid and resinous residues which accumulate in the still-dehydrator (12), part of the reaction mixture is withdrawn through pipe (22) and passed into a mixer (23) into which there are introduced, through (24), the aqueous solutions of maleic acid formed, respectively, in the barometric washers (7) and (18). There is thus formed an aqueous suspension which is withdrawn through discharge pipe (25) by pump (26) and passed to a filter (27), in which there are separated a cake of fumaric acid and resinous residues, which is washed at least once with water supplied through pipe (28), and a filtrate composed of the liquid phase of the said suspension, together with the cake washing waters, and which consists of a maleic acid solution which is recycled through pipe (29) and the pipe (3) to the washer (1). The water supplied through the pipe (28) may be partly or entirely replaced by the aqueous solutions of maleic acid recovered from the barometric washers (7) and (18).

The following Examples are given for the purpose of illustrating the present invention, reference being made to the accompanying drawing:—

Example 1

A benzene oxidation reactor (not shown) produces 2000 moles maleic anhydride per hour, of which 1000 moles per hour are condensed by cooling the gases in condensers (not shown) and 1000 moles per hour are recovered, in the form of an aqueous solution of maleic acid, from the washer (1).

This washer is fed at (3) with an aqueous recycled solution originating from the barometric washers (7) and (18), which contains about 75 moles of recovered maleic acid per hour, together with 125 moles per hour of maleic acid, which are recovered from the purge circuit (22), (23), (25), (26), (27), (29) and (3).

As shown in the drawing, the aqueous solution originating from the barometric washers (7) and (18) serves to dissolve this purged material; after filtration, this solution, which contains 200 moles of maleic acid per hour, is recycled to the washer (1) through the pipes (29) and (3).

The evaporator (5) is thus fed with a concentrated solution containing 450 grams of maleic acid per litre, at the rate of 1200 moles per hour (1000 moles per hour coming from the washing of the gases leaving the maleic anhydride condensers and 200 moles per hour (125+75) recycled at (3)).

The water vaporised from the aqueous solution of maleic acid at a temperature of 135°C. and under a pressure of 500 mm.Hg. in the evaporator (5) escapes through the pipe (6) and is condensed in the barometric washer (7), while the maleic acid, now containing only about 1% by weight of water, leaves at the base of the evaporator at a temperature of 135°C. and is passed through the pipe (11) to the still-dehydrator (12).

The latter, also receiving the 1000 moles per hour of maleic anhydride coming from the condensers (not shown) through the pipe (13), contains a weight of reaction mixture corresponding to four times the hourly quantity by weight of maleic anhydride produced by the reactor, i.e. 8000 moles, calculated as maleic anhydride. The still-dehydrator works at a pressure of 135 mm.Hg. and at a temperature of 135°C.

The condenser (15) condenses, at a temperature of 80°C. , 2000 moles per hour of pure maleic anhydride, from which must be deducted the loss of the purge circuit, which, as a maximum, attains 1.5% by weight. The pure maleic anhydride obtained as product of the process is collected in the liquid state at the base of the condenser (15) through the pipe (16); its maleic anhydride content is 99.5% by weight, its fumaric acid content is practically zero and its content of other impurities is 0.4% by weight. The maleic anhydride thus obtained is passed, if necessary, to a distillation column (not shown) for the removal of the last traces of impurities and for stabilisation.

The water vapour escaping at the top of the condenser (15) is passed through the pipe (17) to the barometric washer (18) connected to a vacuum source (not shown) in order to recover the traces of maleic anhydride entrained by the water vapour; the resulting aqueous solution of maleic acid is either re-

cycled directly to the washer (1) or is preferably used for dissolving the purged product of the still-dehydrator (16), for which purpose it is passed through the pipe (24) to the mixer (23).

5 The composition of the reaction mixture contained in the still-dehydrator, which depends on the rate of dehydration and the amount of the purge effected at (22), amounts, as an average during the duration of the test, to about 5% maleic acid, about 15% fumaric acid, about 78% maleic anhydride and about 2% resinous residues by weight.

10 The purged material (22) is dissolved in the mixer (23) under vacuum and the insoluble material (fumaric acid and resinous residues) is separated on the filter (27), the filter cake being washed with water entering through (28).

20 For dissolution in the mixer (23), use is preferably made of the aqueous solution of maleic acid originating from the recoveries effected at the barometric washers (7) and (18). 200 moles of recovered acid per hour (125 moles originating from the suspension of the purged material and 75 moles originating from the barometric washers (7) and (18)) are thus recycled through (29) and (3) to the washer (1).

30 The filter cake constitutes the loss suffered in the process of the present invention. This loss comprises the maleic acid which was not extracted from the cake by washing and the fumaric acid which was formed from the maleic acid in the course of the dehydration process; it amounts to 1.5%. The duration of the test described in this Example is 330 hours, which corresponds to about four times the length of the same test carried out without effecting the continuous purge according to the present invention. At the moment when the test was stopped, the contents of the various constituents of the reaction mixture in the still-dehydrator were still those indicated in this Example and did not justify suspension of production.

Example 2

50 A butane oxidation pilot reactor (not shown) produces 23 kg. of maleic anhydride per hour, of which 6 kg./hour are condensed by cooling the gases in condensers (not shown) and 17 kg./hour are recovered, in the form of an aqueous solution of maleic acid, from the washer (1).

55 This washer is fed at (3) with an aqueous recycled solution originating from the barometric washers (7) and (18), which contains about 4.11 kg. of recovered maleic acid per hour, together with 5.79 kg./hour of maleic acid, which are recovered from the purge circuit (22), (23), (25), (26), (27), (29) and (3).

60 The aqueous solution originating from the barometric washer (7) via pipe (10) is passed through pipe (24) to dissolve the purged

material in the mixer (23); a total of 9.90 kg. of maleic acid per hour is recycled to the washer (1) through pipes (29) and (3).

70 The evaporator (5) is thus fed with a 38.5% by weight concentrated solution of maleic acid at the rate of 30 kg. per hour (20.1 kg./hour coming from the washing of the gases leaving the maleic anhydride condensers and 9.9 kg./hour recycled at (3)).

75 The water vaporised from the aqueous solution of maleic acid at a temperature of 135°C. and under a pressure of 500 mm.Hg. in the evaporator (5), escapes through the pipe (6) and is condensed in the barometric washer (7), while the maleic acid, now containing only about 1% by weight of water, leaves at the base of the evaporator at a temperature of 135°C. and is passed through the pipe (11) to the still-dehydrator (12).

85 The latter, also receiving the 6 kg./hour of maleic anhydride coming from the condensers (not shown) through the pipe (13), contains a weight of reaction mixture corresponding to four times the hourly quantity by weight of maleic anhydride produced by the reactor, i.e. 125 kg., calculated as maleic anhydride. The still-dehydrator works at a pressure of 135 mm.Hg. and at a temperature of 135°C.

95 The condenser (15) condenses, at a temperature of 80°C., 22.5 kg./hour of pure maleic anhydride. The pure maleic anhydride obtained as product of the process is collected in the liquid state at the base of the condenser (15) through the pipe (16); its maleic anhydride content is 99.5% by weight, its fumaric acid content is practically nil and its content of other impurities reaches 0.4% by weight. If necessary, the maleic anhydride thus obtained is passed to a distillation column (not shown) for the removal of the last traces of impurities and for stabilisation.

105 The water vapour escaping at the top of the condenser (15) is passed through the pipe (17) to the barometric washer (18) connected through (19) to a vacuum source (not shown), in order to recover the traces of maleic anhydride entrained by the water vapour; the resulting aqueous solution of maleic acid is either recycled directly to the washer (1) or is preferably used for dissolving the purged product of the still-dehydrator, for which purpose it is passed through pipes (21) and (24) to the mixer (23).

120 The composition of the reaction mixture contained in the still-dehydrator, which depends on the rate of dehydration and the amount of the purge effected at (22), amounts, as an average during the duration of the test, to about 3% of maleic acid, about 30% of fumaric acid, about 66.5% of maleic anhydride and about 0.5% of resinous residues by weight.

125 The purged material (22) is dissolved in the mixer (23) under vacuum and the in-

soluble material (fumaric acid and resinous residues) is separated on the filter (27), the filter cake being washed with water entering through (28).

- 5 As indicated above, for dissolution in the mixer (23), use is made of the aqueous solutions of maleic acid originating, respectively, from the recoveries effected at the barometric washers (7) and (18). 9.9 kg./hour of recovered acid (5.79 kg./hour originating from the suspension of the purged material and 4.11 kg./hour from the barometric washers (7) and (18) are thus recycled through (29) and (3) to the washer (1).

- 15 The filter cake constitutes the loss suffered in the the process of the present invention. This loss comprises the maleic acid which was not extracted from the cake by washing and the fumaric acid which was formed from the maleic acid in the course of the dehydration process; it amounts to 2%.

- 20 After 480 hours, i.e. at the moment when the test was stopped, the contents of the various constituents of the reaction mixture in the still-dehydrator were still those indicated in this Example and did not justify suspension of production.

WHAT WE CLAIM IS:—

- 30 1. A continuous process for the preparation of maleic anhydride from an aqueous solution of maleic acid formed in the production of maleic anhydride by the catalytic oxidation of aliphatic or aromatic hydrocarbons, with the continuous elimination of the impurities which accompany this maleic acid solution or which are subsequently formed in the course of the conversion of maleic acid into maleic anhydride, which comprises the following stages:

- 40 (a) the starting aqueous solution of maleic acid is continuously heated in a concentration zone kept at a temperature of 100—150°C. and at a pressure of 400—760 mm. Hg. in order to obtain molten maleic acid containing 0—10% by weight of water and water vapour, said water vapour being washed in order to recover the entrained maleic acid, the aqueous solution of maleic acid thus formed being fed to stage (c);

- 50 (b) the molten maleic acid obtained in stage (a) is fed continuously to a conversion zone kept at a temperature of 115—165°C. and at a pressure of 40—200 mm.Hg. and containing, on the one hand, a liquid suspension consisting of a reaction mixture containing 1—20% by weight of maleic acid, 0—30% by weight of fumaric acid, 99—55% by weight of maleic anhydride and 0—5% by weight of resinous residues and, on the other hand, a purified gaseous phase containing maleic anhydride and water vapour, the amount of molten maleic acid added in an hour to the said reaction mix-

ture representing from 10 to 50% of the weight of said reaction mixture;

- (c) part of said reaction mixture, representing from 0.5 to 5% by weight of said reaction mixture per hour, is continuously or semi-continuously taken off and fed to a dissolution and filtration zone, in which it is suspended in the aqueous solution of maleic acid coming from stages (a) and (d), the suspension thus obtained being filtered in order to separate a solid cake of fumaric acid and resinous residues, which is discharged from the system, and a liquid filtrate consisting of an aqueous solution of maleic acid, which is recycled to the starting aqueous solution of maleic acid;

- (d) the gaseous phase produced in stage (b) is continuously condensed at a temperature above the dew point of the water vapour present, the condensate thus obtained being maleic anhydride with a purity of at least 99%, which is collected as the product of the process, while the residual water vapour, which still contains entrained maleic anhydride, is washed with water in order to form an aqueous solution of maleic acid, which is recycled to stage (c).

2. Process according to claim 1, wherein the temperature in the concentration zone is kept at about 135°C.

3. Process according to claim 1 or 2, wherein the pressure in the concentration zone is kept at about 500 mm.Hg.

4. Process according to any of the preceding claims, wherein the residence time in the concentration zone is 0.1 to 5 minutes.

5. Process according to claim 4, wherein the residence time in the concentration zone is less than 1 minute.

6. Process according to claim 1 for the preparation of maleic anhydride, substantially as hereinbefore described and exemplified.

7. Maleic anhydride, whenever prepared by the process according to any of claims 1 to 6.

8. Apparatus for carrying out the process according to claim 1, which comprises a washer connected through a pipe to a source of maleic anhydride and feeding through a pipe an evaporator which is connected through a pipe to a barometric washer and through a pipe to a still-dehydrator, said still-dehydrator being connected (a) through a pipe to a source of maleic anhydride, (b) through a pipe to a maleic anhydride condenser provided with a maleic anhydride discharge pipe and a pipe connecting it with a second barometric washer and (c) through a pipe to a mixer provided, on one hand, with a pipe connecting it to two discharge pipes of the two barometric washers and, on the other hand, with a pipe connecting it to a pump feeding a filter provided with a washing water supply pipe and a filtrate pipe feeding the washer through a pipe.

9. Apparatus according to claim 8, wherein the discharge pipes of the barometric washers are also connected through a pipe to the filter.

- 5 10. Apparatus according to claim 8 for carrying out the process according to claim 1, substantially as hereinbefore described and exemplified and with reference to the accompanying drawing.

VENNER, SHIPLEY & CO.,
Chartered Patent Agents,
Rugby Chambers,
2, Rugby Street,
London, WC1N 3QU.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

1424747

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

